Supporting Information

Charge Density of 4-Methyl-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]thiazole-2(3*H*)-thione. A Comprehensive Multipole Refinement, Maximum Entropy Method and Density Functional Theory Study.

Barbora Vénosová,[1]Julia Koziskova,[1,2] Jozef Kožíšek,[1] Peter Herich,[1] Karol Lušpai,[1] Vaclav Petricek,[2] Jens Hartung,[3] Mike Müller,[3] Christian B. Hübschle,[4] Sander van Smaalen,[4] Lukas Bucinsky[1,]*

[1]*Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food technology, Slovak Technical University of Technology in Bratislava, Radlinského 9, SK-81237 Bratislava, Slovak Republic*

[2] *Institute of Physics, Czech Academy of Sciences, Na Slovance 1999/2, 182 21 Praha 8, Czech Republic*

[3] *Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany*

[4] *Laboratory of Crystallography, University of Bayreuth, Universitätsstrasse 30, 95447 Bayreuth Germany*

**lukas.bucinsky@stuba.sk*

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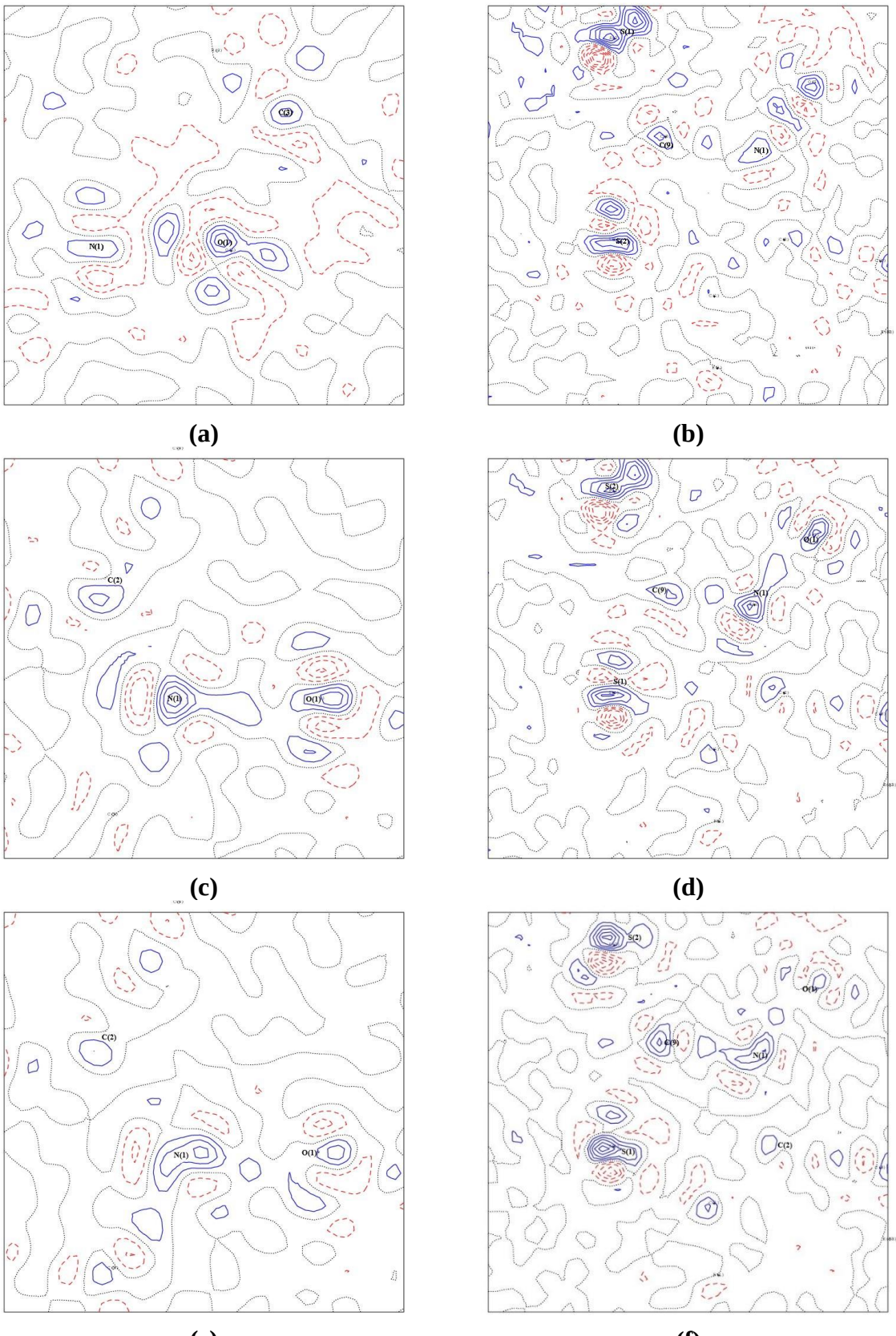
Brief description of the QTAIM method

The distribution of electron density ρ(r) determines the properties of a molecule. An extended analysis of the topology of electron density and thus elucidation of information about the electronic structure can be obtained from the QTAIM analysis. QTAIM provides valuable information about the character of individual bonds in a system, thanks to bond critical points (BCP – distance between BCP and atom A or B). BCP is a point between two atoms on a surface where the gradient (first derivative) of electron density is zero ($\nabla\rho = 0$) and the density is maximal. Three important parameters are characterizing a BCP, i.e. electron density, another useful parameter is the BCP Laplacian (representing the local charge concentration or depletion), and BCP ellipticity ε which describes its deviation from cylindrical symmetry (such as in ideal single or triple bonds) due to its double-bond (π –) character, or mechanical strain, and/or special perturbations/interactions (hydrogen bonds). Delocalization index (DI) (Bader, 1990; Matta & Boyd, 2007) is a useful parameter to quantify bond strength (order) within QTAIM.

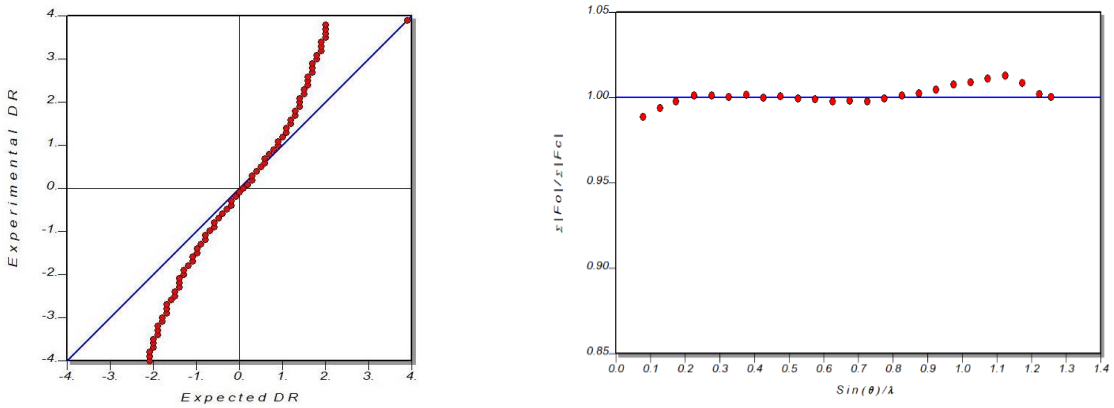


(a) **(b)**

(c) **(d)**

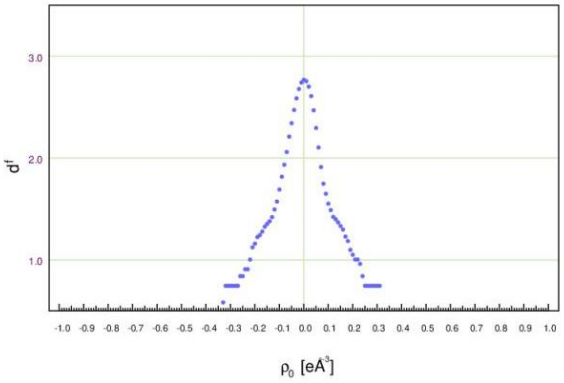
(e) **(f)**

Figure S1. The experimental MM, MM^{Rkeep} and MM^{R} residual density maps in the (a,c,e) N(1)-O(1)-C(3) plane and (b,d,e) in the thiazole-2(3*H*)-thione-nucleus ring [C(9)–S(1)–C(1) plane], respectively. The contours are drawn a 0.05 e/Å^3, positive contours are drawn with a solid blue line, negative contours with a dashed red line and black line is the zero contour



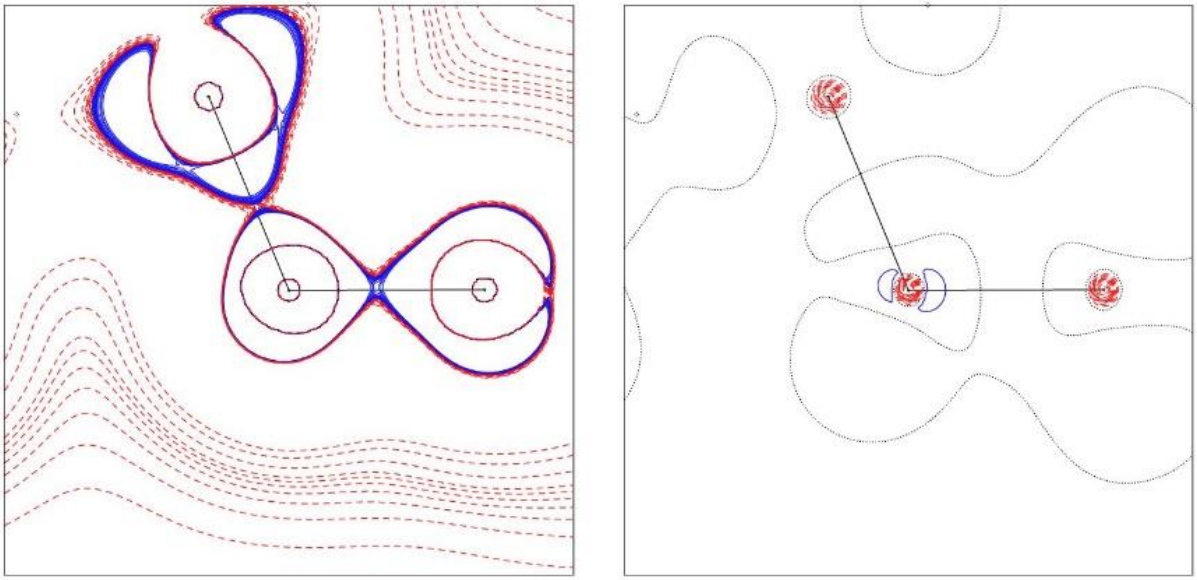
(a)

(b)



(c)

Figure S2. Normal probability distribution plot (a), variation of scale factor with respect to resolution (b), and residual density analysis according to Meindl & Henn (Meindl & Henn, 2008) (c)



(a) **(b)**

Figure S3. Difference counter maps of the BLYP/6-311++G** minus the B3LYP/6-311++G**: (a) Laplacian of the electron density, and (b) electron density in the N(1)–O(1)–C(3) plane. Contours of the Laplacian map are drawn at contours ± 1.0 x 10^{-3}, ± 2.0 x 10^{n}, ± 4.0 x 10^{n} (n = -3, -2, -1, 0, +1, +2, +3) e/$Å^5$, with positive contours drawn with a solid blue line and negative contours with a dashed red line. Electron density contours are drawn at ± 1.0 x 10^{-3}, ± 2.0 x 10^{n}, ± 4.0 x 10^{n} (n = -3, -2, -1, 0, +1, +2, +3) e/$Å^3$

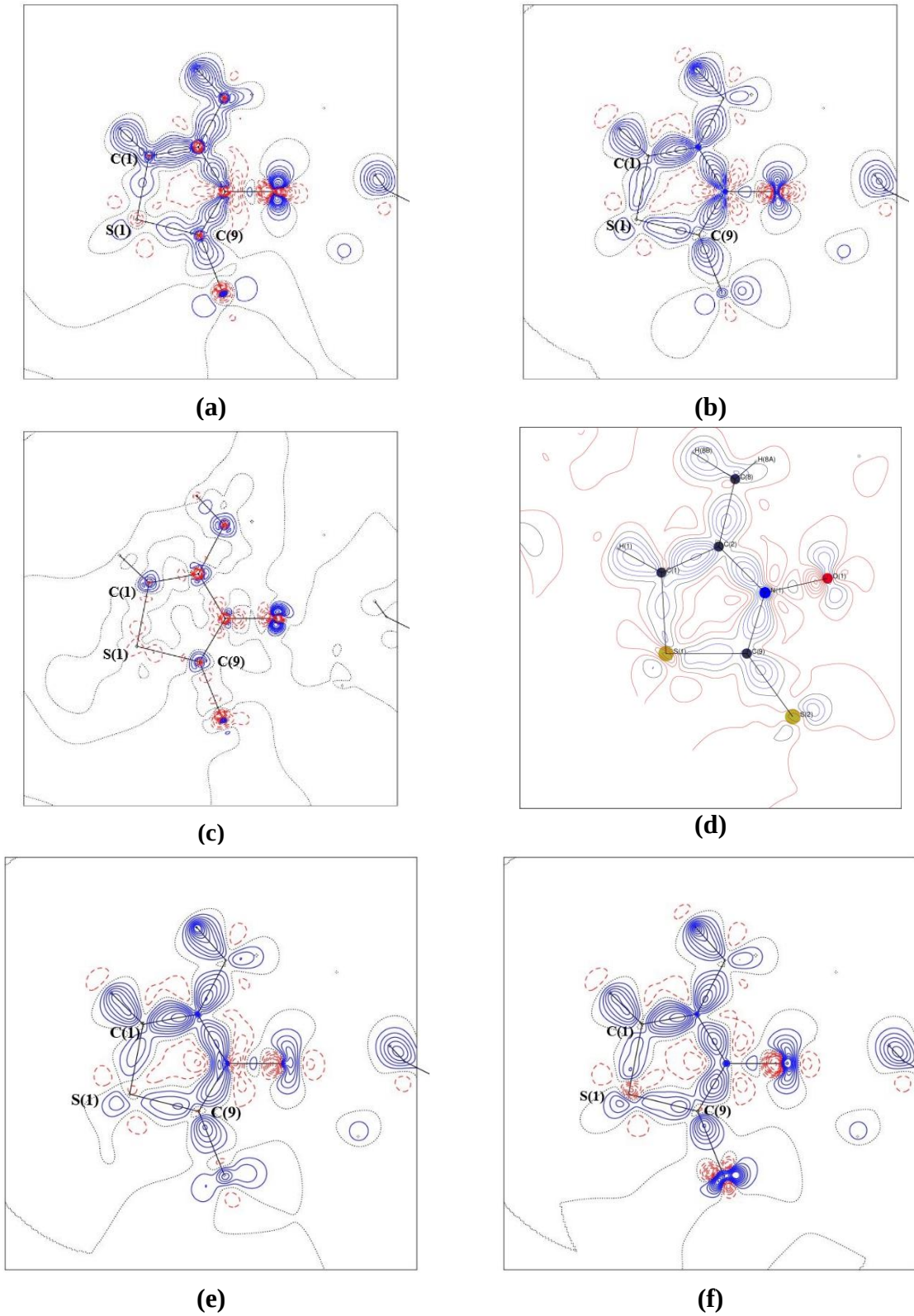
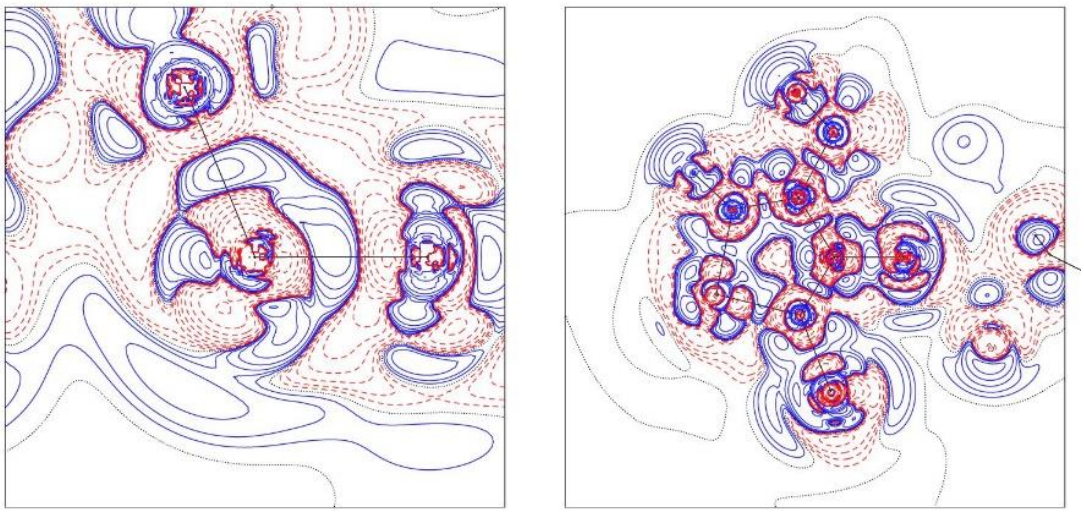
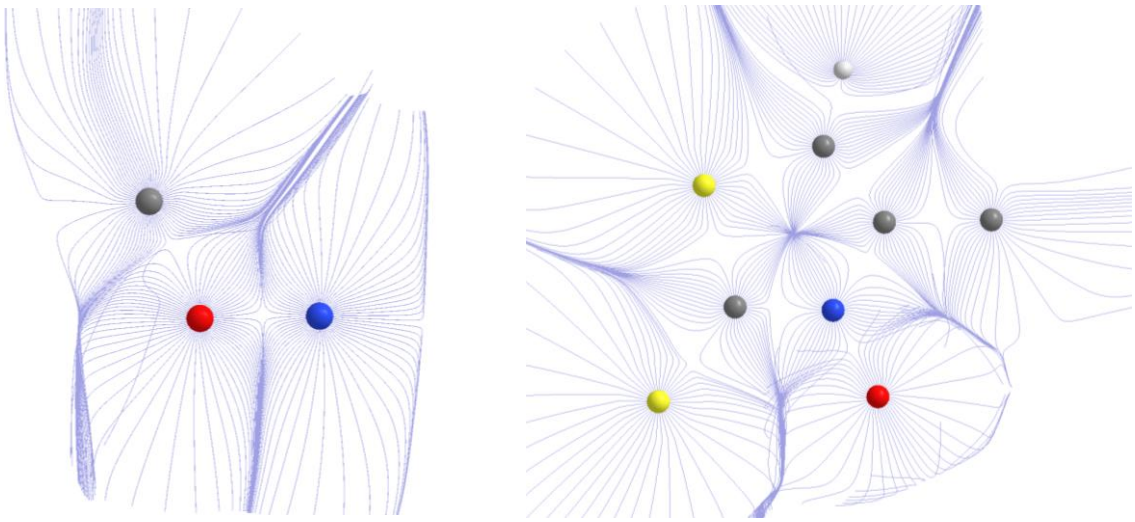


Figure S4. Deformation density and difference deformation density in the thiazole-2(3*H*)-thione-nucleus [C(9)–S(1)–C(1) plane]: (a) BLYP/6-311++G**, (b) experimental MM, (c) BLYP/6-311++G** minus experimental MM, (d) experimental MEM, (e) experimental MM^{Rkeep}, and (f) experimental MM^{R} (contours are drawn at ± 1.0 x 10^{-3}, ± 2.0 x 10^{n}, ± 4.0 x 10^{n} (n = -3, -2, -1, 0, +1, +2, +3) e/Å^{3},)



(a) **(b)**

Figure S5. Difference Laplacian of the electron density (BLYP/6-311++G** minus experimental MM): (a) in the N(1)–O(1)–C(3) plane, and (b) in the C(9)–S(1)–C(1) plane. Contours are drawn at ± 1.0 x 10^{-3}, ± 2.0 x 10^{n}, ± 4.0 x 10^{n} (n = -3, -2, -1, 0, +1, +2, +3) e/Å^{5}, with positive contours drawn with a solid blue line and negative contours with a dashed red line



(a) **(b)**

Figure S6. Atomic basin 2D maps of the electron density gradients in the (a) N(1)-O(1)-C(3) plane and (b) in the thiazole-2(3H)-thione-nucleus ring [C(9)–S(1)–C(1) plane]

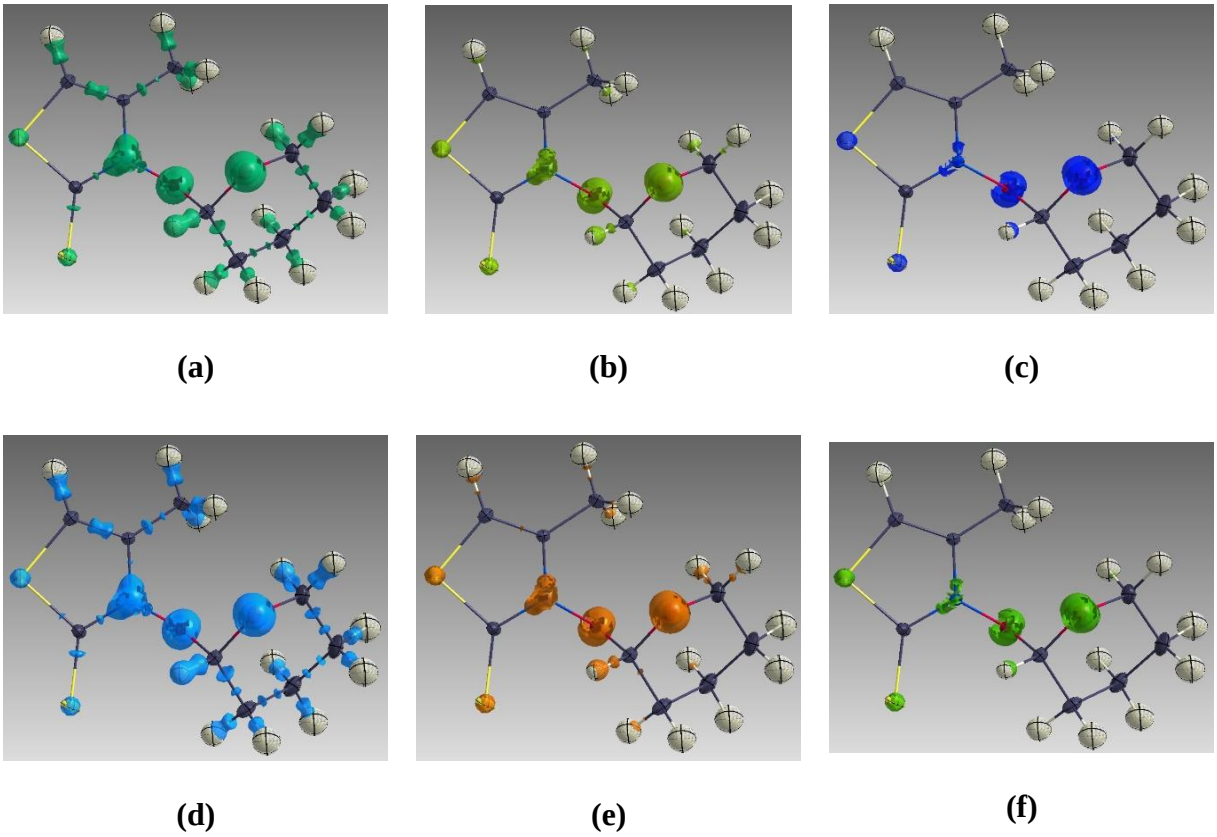
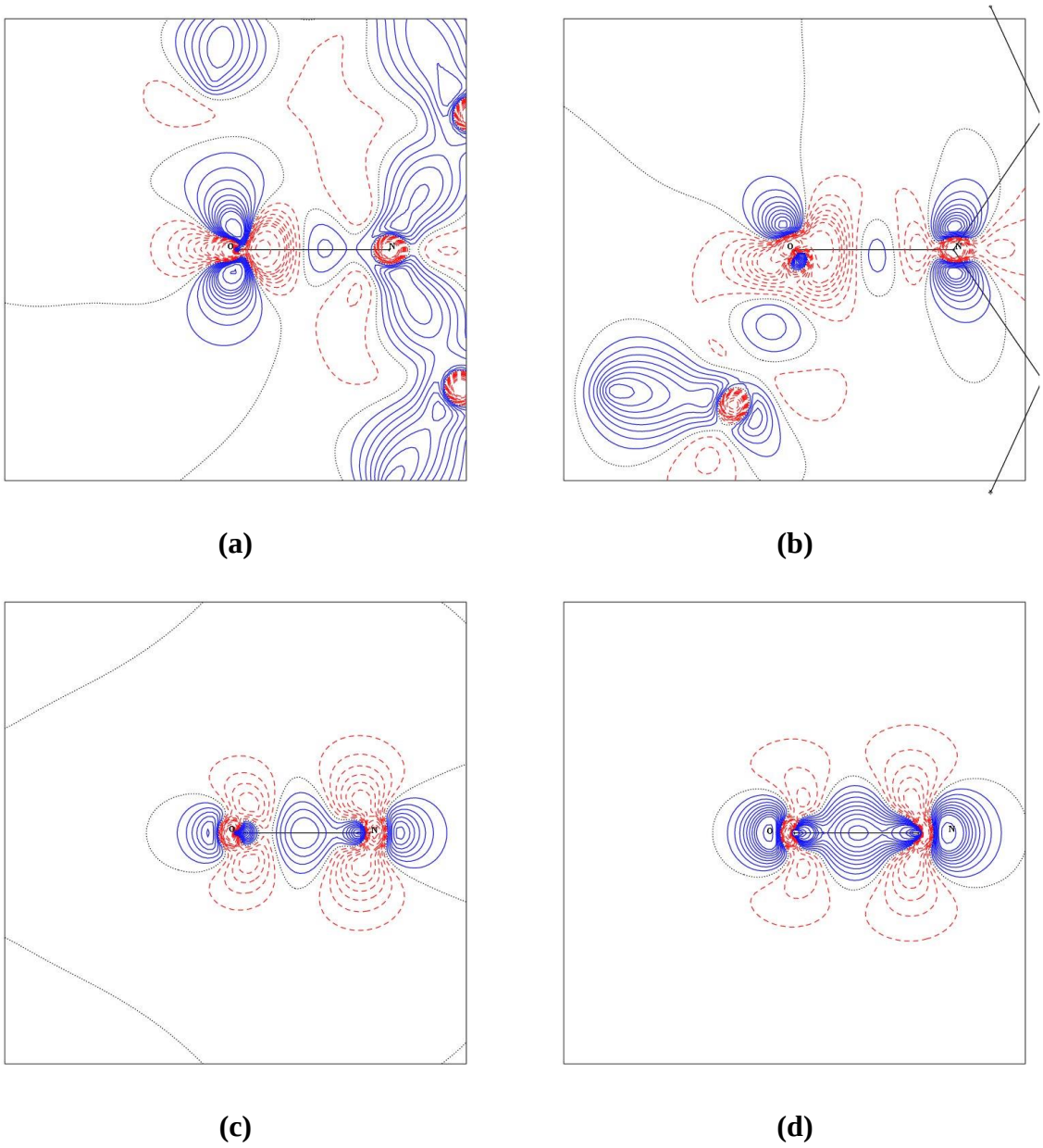


Figure S7. B3LYP/6-311++G** (a-c), and BLYP/6-311++G** (d-f) 3D plots (Hübschle & Dittrich, 2011) of the Laplacian of electron density at the isosurface value of (a. d) 20 e/Å^5, (b, e) 30 e/Å^5 and (c, f) 40 e/Å^5



(a) **(b)**

(c) **(d)**

Figure S8. B3LYP/6-311++G** deformation density maps of N–O bond in (a) **PANO**, (b) $(C_4H_4)NOCH_3$, (c) NO, and (d) NO^+. Contours are drawn at ± 1.0 x 10^{-3}, ± 2.0 x 10^n, ± 4.0 x 10^n (n = -3, -2, -1, 0, +1, +2, +3) e/$Å^3$. Positive contours are drawn with a solid blue line, negative contours with a dashed red line and black line is the zero contour

Table S1. The HAR B3LYP/POB-TVZP averaged anisotropic parameters of heteroatoms and the isotropic thermal smearing of hydrogens and their absolute ($stdev_0$) and relative ($stdev_{0(rel)}$) deviations

Atoms	HAR_{anisoH}	HAR_{isoH}	HAR_{posH}
S(1)	0.015	0.015	0.015
S(2)	0.018	0.018	0.017
O(1)	0.012	0.012	0.011
O(2)	0.014	0.014	0.014
N(1)	0.011	0.011	0.010
C(1)	0.015	0.015	0.016
C(2)	0.012	0.012	0.012
C(3)	0.013	0.013	0.014
C(4)	0.020	0.020	0.021
C(5)	0.023	0.023	0.024
C(6)	0.024	0.023	0.025
C(7)	0.018	0.018	0.019
C(8)	0.016	0.016	0.017
C(9)	0.013	0.013	0.014
$stdev_0$	**0.0011**	**0.0011**	**0.0003**
$stdev_{0(rel)}$	**6.4492**	**6.4989**	**2.4585**
H(1)	0.042	0.040	0.046
H(3)	0.028	0.028	0.022
H(4A)	0.041	0.039	0.035
H(4B)	0.043	0.040	0.047
H(5A)	0.050	0.047	0.063
H(5B)	0.045	0.042	0.027
H(6A)	0.053	0.050	0.041
H(6B)	0.055	0.052	0.039
H(7A)	0.038	0.036	0.030
H(7B)	0.034	0.033	0.037
H(8A)	0.041	0.038	0.032
H(8B)	0.048	0.045	0.047
H(8C)	0.043	0.042	0.039
$stdev_0$	**0.0101**	**0.0092**	**0.0000**
$stdev_{0(rel)}$	**30.0545**	**26.1813**	**0.0000**

Table S2. HAR B3LYP/POB-TVZP bond lengths for two different statistics (equiv and poiss) and two different dataset ranges: sin θ/λ ≤ 1.07 Å^{-1} and sin θ/λ ≤ 1.27 Å^{-1}

Bonds	$HAR_{(posH)}$			
	1.07 equiv [Å]	**1.27 equiv* [Å]**	**1.07 poiss [Å]**	**1. 27 poiss [Å]**
S(1)–C(1)	1.733	1.733	1.733	1.733
S(1)–C(9)	1.732	1.732	1.732	1.733
S(2)–C(9)	1.669	1.669	1.669	1.669
O(1)–N(1)	1.377	1.376	1.375	1.377
O(1)–C(3)	1.474	1.473	1.474	1.474
O(2)–C(3)	1.389	1.389	1.389	1.389
O(2)–C(7)	1.445	1.445	1.445	1.445
N(1)–C(2)	1.396	1.396	1.396	1.396
N(1)–C(9)	1.360	1.360	1.360	1.360
C(1)–C(2)	1.352	1.354	1.353	1.352
C(2)–C(8)	1.487	1.486	1.486	1.486
C(3)–C(4)	1.521	1.522	1.521	1.521
C(4)–C(5)	1.532	1.532	1.533	1.531
C(5)–C(6)	1.530	1.532	1.531	1.530
C(1)–H(1)	1.064	1.065	1.081	1.096
C(3)–H(3)	1.089	1.090	1.110	1.117
C(4)–H(4A)	1.095	1.095	1.122	1.123
C(4)–H(4B)	1.105	1.104	1.132	1.136
C(5)–H(5A)	1.093	1.092	1.127	1.127
C(5)–H(5B)	1.107	1.110	1.107	1.119
C(6)–H(6A)	1.105	1.103	1.142	1.139
C(6)–H(6B)	1.096	1.097	1.127	1.131
C(7)–H(7A)	1.111	1.110	1.117	1.115
C(7)–H(7B)	1.081	1.083	1.107	1.108
C(8)–H(8A)	1.081	1.084	1.096	1.107
C(8)–H(8B)	1.084	1.085	1.083	1.091
C(8)–H(8C)	1.089	1.090	1.109	1.109
$stdev_0$	**0.0106**	**0.0117**	**0.0290**	**0.03014**

*the 1.27 equiv experimental data is considered in the manuscript (if not otherwise stated)

Table S3. The comparison of C–H bond lengths from HAR against neutron dataset reference (four columns EXP for the calculated bond lengths from Tonto HAR B3LYP/POB-TVZP and from the optimized geometry from CRYSTAL17 B3LYP/ POB-TVZP, respectively); and the comparison against the optimized CRYSTAL17 B3LYP/ POB-TVZP C–H bond lengths (three columns OPT for the Tonto HAR B3LYP/POB-TVZP bond lengths)

Reference:	**EXP**				**OPT**		
bonds	**HAR_{anisoH}**	**HAR_{isoH}**	**HAR_{posH}**	**OPT**	**HAR_{anisoH}**	**HAR_{isoH}**	**HAR_{posH}**
C(1)–H(1)	-0.018	-0.020	-0.018	-0.007	-0.011	-0.013	-0.011
C(3)–H(3)	-0.011	-0.012	-0.007	-0.014	0.003	0.002	0.006
C(4)–H(4A)	0.002	0.003	0.003	-0.003	0.005	0.006	0.006
C(4)–H(4B)	0.008	0.008	0.012	0.001	0.007	0.007	0.011
C(5)–H(5A)	0.000	0.002	0.000	-0.001	0.001	0.003	0.001
C(5)–H(5B)	0.006	0.009	0.018	0.000	0.007	0.010	0.018
C(6)–H(6A)	0.010	0.003	0.010	0.000	0.010	0.003	0.011
C(6)–H(6B)	-0.005	0.000	0.005	-0.001	-0.005	0.000	0.006
C(7)–H(7A)	0.011	0.018	0.018	-0.005	0.015	0.023	0.023
C(7)–H(7B)	-0.009	-0.015	-0.008	-0.003	-0.006	-0.012	-0.006
C(8)–H(8A)	0.006	0.005	0.007	0.011	-0.004	-0.006	-0.004
C(8)–H(8B)	0.011	0.014	0.007	0.011	0.000	0.004	-0.003
C(8)–H(8C)	0.006	0.011	0.013	0.013	-0.007	-0.003	0.000
$stdev_0$	**0.0094**	**0.0114**	**0.0117**	**0.0076**	**0.0078**	**0.0094**	**0.0107**

Table S4. ADPs from SHADE3 and HAR

Atoms	SHADE			HAR		
	U_{11}	U_{22}	U_{33}	U_{11}	U_{22}	U_{33}
S(1)	0.0102(3)	0.01851(4)	0.01757(4)	0.010	0.018	0.017
S(2)	0.01996(4)	0.01887(4)	0.01490(4)	0.020	0.019	0.015
O(1)	0.01162(9)	0.00965(8)	0.01318(10)	0.013	0.010	0.013
O(2)	0.01138(9)	0.01216(9)	0.01692(11)	0.012	0.013	0.017
N(1)	0.00964(9)	0.01014(9)	0.01126(10)	0.010	0.010	0.011
C(1)	0.01429(12)	0.01399(13)	0.01563(14)	0.014	0.014	0.016
C(2)	0.01219(11)	0.01090(11)	0.01105(11)	0.012	0.011	0.012
C(3)	0.01358(12)	0.01230(12)	0.01208(12)	0.014	0.012	0.013
C(4)	0.02306(17)	0.01487(14)	0.01987(16)	0.023	0.015	0.020
C(5)	0.02407(18)	0.01506(15)	0.0282(2)	0.024	0.015	0.028
C(6)	0.01604(15)	0.02292(18)	0.0312(2)	0.016	0.023	0.031
C(7)	0.01234(12)	0.01915(15)	0.02069(16)	0.013	0.019	0.021
C(8)	0.01521(13)	0.01833(14)	0.01530(14)	0.015	0.019	0.016
C(9)	0.01141(11)	0.01347(12)	0.01229(12)	0.012	0.014	0.012
H(1)	0.015063	0.013157	0.014306	0.048	0.032	0.046
H(3)	0.01149	0.013107	0.010058	0.024	0.035	0.028
H(4A)	0.010237	0.011537	0.023297	0.041	0.026	0.056
H(4B)	0.017258	0.018429	0.008845	0.040	0.051	0.036
H(5A)	0.014755	0.010531	0.019672	0.061	0.025	0.062
H(5B)	0.014056	0.02265	0.007982	0.049	0.042	0.042
H(6A)	0.018894	0.015439	0.010101	0.050	0.047	0.059
H(6B)	0.015907	0.014769	0.014763	0.040	0.047	0.080
H(7A)	0.011864	0.009835	0.023336	0.023	0.036	0.057
H(7B)	0.016154	0.020057	0.008373	0.032	0.046	0.025
H(8A)	0.011713	0.03397	0.014627	0.025	0.054	0.043
H(8B)	0.019966	0.020986	0.01979	0.052	0.050	0.043
H(8C)	0.024273	0.01009	0.026839	0.051	0.032	0.048
Atoms	U_{12}	U_{13}	U_{23}	U_{12}	U_{13}	U_{23}
S(1)	0.00211(3)	0.00127(3)	-0.00100(3)	0.002	0.001	-0.001
S(2)	-0.00555(3)	0.00392(3)	0.00363(3)	-0.005	0.004	0.004
O(1)	0.00190(7)	-0.00222(7)	-0.00121(7)	0.000	-0.001	-0.001
O(2)	0.00050(7)	-0.00039(8)	-0.00414(8)	0.001	-0.002	-0.004
N(1)	0.00046(7)	0.00046(8)	0.00098(8)	0.000	0.000	0.001
C(1)	0.00222(10)	-0.00071(10)	0.00182(10)	0.003	-0.001	0.002
C(2)	-0.00007(9)	0.00024(9)	0.00114(9)	0.000	0.001	0.001

C(3)	0.00116(9)	-0.00234(10)	-0.00068(9)	0.002	-0.002	-0.001
C(4)	0.00395(12)	-0.00547(13)	0.00290(12)	0.004	-0.005	0.003
C(5)	0.00779(13)	-0.00614(15)	-0.00409(13)	0.008	-0.006	-0.004
C(6)	0.00823(13)	-0.00370(14)	-0.00647(15)	0.008	-0.004	-0.006
C(7)	0.00264(11)	0.00102(11)	-0.00436(12)	0.002	0.000	-0.004
C(8)	-0.00027(11)	0.00368(11)	0.00421(11)	0.000	0.004	0.004
C(9)	-0.00200(9)	0.00117(9)	-0.00072(9)	-0.002	0.002	0.000
H(1)	0.003939	0.000876	0.008432	0.013	0.001	0.015
H(3)	0.002367	0.004423	-0.002833	0.006	0.008	-0.005
H(4A)	-0.004677	0.003264	0.00027	-0.004	-0.001	0.013
H(4B)	0.002991	-0.005491	-0.003158	0.011	-0.020	0.001
H(5A)	0.004667	0.001463	0.006277	0.020	-0.010	0.001
H(5B)	-0.003169	-0.003052	-0.002543	0.006	-0.018	-0.015
H(6A)	-0.002337	-0.007019	-0.000489	0.005	-0.026	-0.003
H(6B)	0.002154	0.009112	-0.001116	0.018	0.022	-0.015
H(7A)	-0.004858	0.002711	-0.000491	-0.007	0.011	0.001
H(7B)	0.00298	-0.004689	-0.003348	0.007	-0.005	-0.012
H(8A)	-0.007418	-0.004257	-0.004927	-0.014	-0.008	0.001
H(8B)	0.006495	0.002899	0.014174	0.002	0.009	0.026
H(8C)	-0.000425	0.010445	-0.008465	0.011	0.016	-0.010

Table S5. B3LYP/POB-TZVP QTAIM charges for periodic and *in vacuo* calculations (experimental geometry), B3LYP/6-311++G** QTAIM charges for SHADE and HAR geometries and for experimental MM^{Rkeep} and MM^{R} calculations

atom	periodic	*in vacuo*	shade	HAR	MM^{Rkeep}	MM^{R}
S(1)	0.893	0.829	0.288	0.289	0.188	0.188
S(2)	0.123	0.150	0.039	0.038	0.013	-0.113
O(1)	-0.602	-0.589	-0.628	-0.634	-0.641	-0.578
O(2)	-0.975	-0.972	-1.042	-1.051	-1.028	-0.919
N(1)	-0.613	-0.599	-0.662	-0.656	-0.654	-0.470
C(1)	-0.477	-0.440	-0.185	-0.175	-0.210	-0.143
C(2)	0.221	0.346	0.381	0.382	0.282	0.206
C(3)	0.682	0.787	0.863	0.877	0.721	0.709
C(4)	0.053	0.065	0.052	0.048	0.045	0.008
C(5)	0.044	0.063	0.054	0.051	-0.034	0.102
C(6)	0.054	0.063	0.053	0.050	-0.053	0.007
C(7)	0.343	0.422	0.449	0.454	0.301	0.333
C(8)	0.126	0.088	0.070	0.058	0.121	0.047
C(9)	-0.587	-0.418	-0.002	-0.005	0.270	0.010
H(1)	-0.251	0.062	0.076	0.069	-0.167	0.162
H(3)	-0.257	0.078	0.078	0.074	0.169	0.188
H(4A)	-0.251	0.032	0.036	0.038	0.127	0.088
H(4B)	-0.251	-0.003	0.001	0.004	0.109	0.027
H(5A)	-0.280	-0.010	-0.006	-0.005	-0.046	-0.086
H(5B)	-0.302	-0.007	-0.003	0.000	-0.265	-0.006
H(6A)	-0.263	-0.011	-0.009	-0.006	0.131	0.075
H(6B)	-0.254	-0.012	-0.008	-0.011	-0.249	-0.064
H(7A)	-0.286	0.015	0.020	0.024	0.098	0.104
H(7B)	-0.275	0.000	0.002	0.000	-0.033	0.006
H(8A)	-0.280	0.034	0.040	0.042	0.092	0.064
H(8B)	-0.287	0.007	0.016	0.020	0.170	0.047
H(8C)	-0.266	0.019	0.026	0.027	0.133	0.033

Table S6. QTAIM BCPs descriptors of $MM^{R_{keep}}$ and MM^{R} derived charge density

$MM^{R_{keep}}$								
Bonds	**A-BCP [Å]**	**BCP-B [Å]**	**ρ [e/Å^3]**	**$\nabla^2\rho$ [e/Å^5]**	**Hessian eigenvalues [e/Å^5]**			**ε**
					λ_1	**λ_2**	**λ_3**	
C(1)–S(1)	0.904	0.830	1.37(12)	-6.151(33)	-8.16	-6.57	8.57	0.24
C(9)–S(1)	0.828	0.906	1.41(11)	-5.687(32)	-8.42	-6.78	9.51	0.24
C(9)–S(2)	0.919	0.749	1.48(12)	-8.645(34)	-6.39	-5.56	3.31	0.15
O(1)–N(1)	0.709	0.665	2.22(23)	-0.784(96)	-17.39	-16.12	32.73	0.08
O(1)–C(3)	0.880	0.595	1.55(10)	-8.233(34)	-10.69	-10.3	12.76	0.04
O(2)–C(3)	0.837	0.554	1.94(12)	-16.452(47)	-14.73	-14.19	12.47	0.04
C(7)–O(2)	0.579	0.867	1.61(12)	-9.727(41)	-11.00	-10.55	11.83	0.04
C(2)–N(1)	0.576	0.821	2.07(15)	-19.788(45)	-16.98	-14.28	11.47	0.19
N(1)–C(9)	0.797	0.565	2.20(15)	-19.917(49)	-17.19	-15.18	12.45	0.13
C(2)–C(1)	0.716	0.637	2.28(9)	-20.892(27)	-18.28	-14	11.39	0.31
C(8)–C(2)	0.692	0.792	1.73(8)	-11.949(18)	-12.31	-11.31	11.67	0.09
C(4)–C(3)	0.732	0.789	1.68(7)	-10.497(16)	-11.45	-11.27	12.23	0.02
C(5)–C(4)	0.790	0.742	1.60(8)	-9.038(16)	-10.66	-10.42	12.04	0.02
C(6)–C(5)	0.815	0.717	1.59(9)	-8.820(19)	-10.49	-10.1	11.77	0.04
C(6)–C(7)	0.739	0.776	1.71(8)	-11.650(16)	-12.26	-11.44	12.04	0.07
MM^{R}								
Bonds	**A-BCP [Å]**	**BCP-B [Å]**	**ρ [e/Å^3]**	**$\nabla^2\rho$ [e/Å^5]**	**Hessian eigenvalues [e/Å^5]**			**ε**
					λ_1	**λ_2**	**λ_3**	
C(1)–S(1)	0.931	0.803	1.38(19)	-4.723(53)	-8.62	-7.06	10.96	0.22
C(9)–S(1)	0.820	0.914	1.42(20)	-4.933(56)	-8.97	-7.16	11.20	0.25
C(9)–S(2)	0.886	0.783	1.41(16)	-2.945(159)	-6.41	-5.79	9.25	0.11
O(1)–N(1)	0.710	0.665	2.23(26)	-1.169(116)	-17.83	-16.31	32.97	0.09
O(1)–C(3)	0.883	0.591	1.55(10)	-8.017(34)	-10.55	-10.02	12.56	0.05
O(2)–C(3)	0.873	0.515	1.90(13)	-17.217(58)	-13.97	-13.07	9.82	0.07
C(7)–O(2)	0.527	0.915	1.56(14)	-9.698(51)	-9.63	-8.90	8.83	0.08
C(2)–N(1)	0.549	0.847	2.05(14)	-20.811(42)	-16.50	-13.84	9.53	0.19
N(1)–C(9)	0.843	0.517	2.17(14)	-22.486(50)	-16.41	-14.88	8.81	0.10
C(2)–C(1)	0.715	0.638	2.29(8)	-21.037(24)	-18.49	-14.01	11.47	0.32
C(8)–C(2)	0.691	0.794	1.73(7)	-11.805(17)	-12.18	-11.29	11.66	0.08
C(4)–C(3)	0.728	0.793	1.68(7)	-10.314(15)	-11.36	-11.29	12.34	0.01
C(5)–C(4)	0.787	0.745	1.60(7)	-8.680(15)	-10.49	-10.30	12.11	0.02
C(6)–C(5)	0.814	0.718	1.59(8)	-8.636(18)	-10.44	-10.09	11.89	0.03
C(6)–C(7)	0.739	0.777	1.71(7)	-11.256(15)	-12.09	-11.36	12.19	0.06

Table S7. QTAIM BCP descriptors from B3LYP/6-311++G** electron density of selected reference C–C bonds

Molecules	ρ [e/Å^3]	∇^2 ρ [e/Å^5]	ε	DI	Hessian eigenvalues [e/Å^5]		
					λ_1	λ_2	λ_3
Ethan	1.676	-14.098	0.000	1.020	-11.265	-11.265	8.8431
Ethen	2.345	-25.289	0.330	1.904	-18.224	-13.668	6.602
Ethyn	2.835	-31.228	0.000	2.854	-16.687	-16.687	2.146
Benzene	2.095	-21.005	0.201	1.391	-15.731	-13.103	7.830

Table S8. QTAIM BCP descriptors from B3LYP/6-311++G** electron density of selected reference N–O bonds

Molecules	N-BCP [Å]	BCP-O [Å]	ρ [e/Å^3]	∇^2ρ [e/Å^5]	Hessian eigenvalues [e/Å^5]			ε	DI
					λ_1	λ_2	λ_3		
NO	0.465	0.683	3.968	-47.441	-37.666	-34.500	24.725	0.092	2.409
NO^+	0.398	0.662	5.006	-62.601	-52.979	-52.979	43.356	0.000	2.603
$(CH_3)_2NOCH_3$	0.673	0.775	1.915	-6.345	-15.534	-15.033	24.221	0.033	1.102
$(CH_3)_2NOH$	0.673	0.779	1.881	-6.042	-15.236	-14.678	23.872	0.038	1.137
CH_2NOCH_3	0.642	0.751	2.183	-10.268	-18.503	-17.895	26.130	0.034	1.216
CH_2NOH	0.632	0.748	2.240	-11.660	-18.897	-18.578	25.815	0.017	1.247
$(C_4H_4)NOCH_3$	0.648	0.733	2.260	-11.538	-19.358	-18.883	26.704	0.025	1.164
$(C_4H_4)NOH$	0.648	0.733	2.222	-11.533	-19.042	-18.476	25.985	0.031	1.190

Table S9. QTAIM BCPs descriptors and DIs from BLYP/6-311++G** electron density

Bonds	A-BCP [Å]	BCP-B [Å]	ρ [e/Å^3]	$\nabla^2\rho$ [e/Å^5]	Hessian eigenvalues [e/Å^5]			ε	DI
					λ_1	λ_2	λ_3		
C(1)–S(1)	0.905	0.829	1.386	-8.879	-7.951	-6.640	5.712	0.197	1.208
C(9)–S(1)	0.894	0.840	1.406	-9.109	-8.227	-6.673	5.791	0.233	1.195
C(9)–S(2)	0.676	0.993	1.424	-4.408	-4.800	-4.705	5.097	0.020	1.586
O(1)–N(1)	0.653	0.725	2.244	-9.327	-19.147	-18.441	28.262	0.038	1.159
C(3)–O(1)	0.913	0.563	1.539	-9.737	-10.353	-9.745	10.361	0.062	0.774
O(2)–C(3)	0.891	0.501	1.870	-14.046	-13.962	-12.576	12.491	0.110	0.891
C(7)–O(2)	0.915	0.531	1.622	-10.810	-10.460	-10.236	9.886	0.022	0.874
C(2)–N(1)	0.878	0.517	1.954	-16.800	-13.918	-12.082	9.200	0.152	1.001
N(1)–C(9)	0.857	0.503	2.109	-18.132	-15.583	-13.324	10.775	0.170	1.109
C(2)–C(1)	0.662	0.690	2.211	-21.567	-16.923	-12.467	7.823	0.357	1.549
C(8)–C(2)	0.776	0.709	1.729	-14.540	-11.913	-11.363	8.736	0.048	1.009
C(4)–C(3)	0.793	0.727	1.694	-13.861	-11.708	-11.507	9.355	0.017	0.928
C(5)–C(4)	0.771	0.761	1.602	-12.171	-10.619	-10.552	9.000	0.006	0.974
C(6)–C(5)	0.762	0.769	1.610	-12.308	-10.677	-10.670	9.039	0.001	0.974
C(6)–C(7)	0.743	0.773	1.687	-13.676	-11.637	-11.340	9.301	0.026	0.967

Table S10. B3LYP/6-311G* LOC orbitals. Atomic orbital s, p_x, p_y, p_z populations and atomic populations of particular atoms in the C(3)–O(1) and N(1)–O(1) bonding LOC orbitals in [*e*]

	AO populations					**LOC_{Atom}**	
Atoms	**s O(1)**	**p_z O(1)**	**p_y O(1)**	**s C(3)**	**p_z C(3)**	**O(1)**	**C(3)**
C(3)–O(1)	0.20	1.14	0.06	0.12	0.48	1.40	0.60
	s O(1)	**p_z O(1)**	**p_y O(1)**	**s N(1)**	**p_z N(1)**	**O(1)**	**N(1)**
N(1)–O(1)	0.08	0.92	-	0.30	0.70	1.00	1.00

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